Safe Handling of Cryogens
I

Introduction

This supplement is designed to describe the principal hazards and appropriate safety procedures associated with four cryogens that are commonly used at LLNL: liquid N_2, He, Ar, and CO_2. Other cryogens, such as liquid O_2, H_2, NH_3, and fluorine, are used only infrequently at this Laboratory and will not be discussed here, though they may pose extreme toxicity, flammability, or other hazards. If you anticipate using cryogens not discussed in this supplement, contact Hazards Control for specific information on safe handling procedures.

An extensive list of useful references is provided at the end of this supplement. Users of cryogenic systems are encouraged to investigate further the safety aspects of cryogens by consulting these references and the current literature, especially when using large systems or exotic cryogenic fluids.

Basic Considerations

Because all cryogenic fluids exist as liquids only at temperatures considerably below ambient, normal storage facilities and fluid containment in process systems must allow for the unavoidable heat input from the environment. For ordinary operations this means good insulation, adequate pressure-relief devices, and proper disposal or recycling of the gases that are continually produced. Full containment of the fluid as a liquid at room temperature is usually not feasible: the pressure required to maintain helium at liquid density at room temperature is 18,000 psi (124,000 kPa); for nitrogen it is 43,000 psi (296,000 kPa).

The chemical properties and reaction rates of substances are changed under cryogenic conditions. Liquid oxygen, for example, will react explosively with materials usually considered to be noncombustible. Remember that condensing a cryogen from a pure gas at room temperature will concentrate the material typically 700–800 times.

Material properties are drastically affected by cryogenic temperatures: ductile materials become brittle, material shrinkage exceeds anticipated values, leaks can develop that are not detectable at room temperature even under considerable pressure, etc. Hence, the suitability of materials must be carefully investigated before they are employed in cryogenic service.

Labeling and Posting

Storage dewars, process vessels, piping, etc., shall be labeled with the common name of the contents. In many cases, it is also desirable to post emergency instructions, emergency call numbers, etc.

Pressure Buildup and Relief

Heat flux into the cryogen is unavoidable, regardless of the quality of the insulation provided. Pressure relief *must* be provided to permit routine off-gassing of the vapors generated by this heat input. Typically such relief is best provided by spring-loaded relief devices or an open passage to the atmosphere.

Additional relief devices should be provided as backup to the operational relief, especially when the capacity of the operational relief device is not adequate to take care of unusual or accident conditions. This may be the case if the insulation is dependent on the maintenance of a vacuum in any part of the system (this includes permanently sealed dewars), if the system may be subject to an external fire, or if rapid exothermic reactions are possible in the cryogen or a container cooled by the cryogen. In each case, relief devices capable of handling the maximum volume of gas that could be produced under the most adverse conditions *must* be provided. Frangible disks are recommended for this service.

Each and every portion of the cryogenic system *must* have uninterruptible pressure relief. Any part of the system that can be valved off from the remainder *must* have separate and adequate provisions for pressure relief. Examples of parts that usually require separate relief systems include the following:

- Pressurized supply dewars;
- Tubing and hoses used to transfer cryogen, unless an air gap is provided;
- Bath space surrounding experimental volume;

- Experimental volume, even if cryogen is in contact with only the exterior; and
- Vacuum spaces in contact with cryogen.

Pressure relief devices *must* be provided in the last two cases because cracks may develop at cryogenic temperatures. Cryogen or air may leak into sealed spaces through such cracks. Some atmospheric gases will condense under such conditions and exist as a cryogen in the sealed space as well. Upon warming, these cracks may close and the contained vaporizing fluid can then shatter the vessel.

All parts in contact with the fluid shall be rated for cryogenic service. Although some economy can be achieved by using ordinary pressure system parts on sections that are thermally isolated from the fluid, this practice is advisable only when performed by an experienced cryogenic engineer.

Each part of the system must be engineered for pressure in accordance with Chapter 32 and Supplement 32.03 of the *Health & Safety Manual*. Pressure-relief devices shall not be set higher than the Maximum Allowable Working Pressure. It is further required that this pressure rating can be met with the usual safety factor at the temperature of minimum strength. Careful consideration must be given to material compatability with respect to prevention of embrittlement at cryogenic temperatures.

Hazards of Oxygen Deficiency

Liquefied gases frequently have a significant potential for creating an oxygen deficiency. When expelled to the atmosphere at room temperature, they evaporate and expand on the order of 700–800 times their liquid volume. Consequently, leaks of even small quantities of liquefied gas can expand to displace large amounts of oxygen, thereby rendering an atmosphere lethal. Without adequate oxygen, one can lose consciousness in a few seconds and die of asphyxiation in a few minutes.

Calculations shall be made to determine whether a given situation of cryogen storage or use will pose an oxygen-deficiency hazard in the event of the worst possible accident. Where cryogen use requires remote piping to an area, special care must be taken to examine the piping to determine whether or not tunnels, pits, or trenches can develop an oxygen deficiency from a broken line. When the level of hazard potential has been ascertained, appropriate safety procedures must be taken. This may require designating the area as a confined space and, in turn, complying with the safety provisions of Supplement 26.14 of the *Health & Safety Manual.*

Where the danger is sufficient to warrant it, this may entail the installation of oxygen-deficiency sensors wired to audible alarms and the Fire Department. Positions for oxygen-deficiency-sensing heads should include the lowest point in the area because the cold, dense, escaping gases will be heavier than the warmer ambient air, at least initially. All employees working in the vicinity of an area where an oxygen deficiency could develop shall be trained as to the nature of the hazard and the appropriate response they should make in the event of cryogen release. Along with training, these areas shall be posted to remind the workers and alert visitors in the area to the hazard and the proper emergency procedures.

Ventilation can also be used to minimize the potential for creating an oxygen deficiency and provide more escape time for people present during a cryogen leak. When routine bleed-off of relief devices could produce an oxygen deficiency inside the building, it should be vented to the exterior.

If dry ice or a dewar containing cryogenic fluid must be transported by elevator, it shall *not* be accompanied by personnel. In case of power failure, an excessive amount of cryogen could vaporize and escape into the cab, leaving personnel with no means of escape and no method of ventilating the cab. Instead, the load shall be sent by itself, and measures shall be taken to assure that no passengers are loaded on intervening floors.

Any rescue work conducted in an oxygen-deficient atmosphere must be done in self-contained breathing apparatus or airline equipment with a self-contained escape unit.

Hazards of Air-Freezing Cryogens

Certain cryogens, such as helium and hydrogen, are cold enough to solidify atmospheric air. Entry of air into such cryostats must be prevented by pressurizing the system. If openings to the atmosphere exist, they are likely to become plugged by solidified air, leading to overpressure and vessel failure if they are relied on for pressure relief. Such conditions will also result in hazardous contamination of the fluid. Again, adequate pressure-relief devices *must* be provided to vent all gas produced in case of maximum possible heat flux into the system.

Unless these fluids are handled in vacuum-jacketed vessels and piping, air will also condense on the exterior of the system. This condensate will be rich in oxygen content. The hazards created by this include frostbite from touching the cold surfaces, dripping liquid air (because it is oxygen-enriched), and exploding insulation. The latter can happen when air condenses between the metal surface and the insulating layer. On warming, the air vaporizes and can rip off the insulation with explosive force. Such insulation systems must be specially engineered to prevent air penetration.

Hazards of Carbon Dioxide (CO_2) Toxicity

In addition to producing an oxygen deficiency, CO_2 also affects the breathing rate because of its role in the respiratory process. A concentration of 0.5% CO_2 in the air will begin to stimulate a more rapid breathing rate; when 3% CO_2 is present in the air, lung ventilation will double; 10% CO_2 can be tolerated for only a few minutes. A condition of 10% CO_2 and 90% normal air actually has an oxygen concentration of 18.9%. This degree of oxygen deficiency would not be considered immediately dangerous to life or health if the contaminant gas was N_2, He, or Ar instead of CO_2. Obviously it is important to measure the CO_2 concentration, especially if it is suspected that this gas may be present at levels greater than 0.5%.

As with oxygen-deficient atmospheres, rescue operations conducted in atmospheres with excessively high CO_2 concentrations must be done only in self-contained breathing apparatus or in a combination of airline respirator equipment and self-contained escape device.

Hazards of Oxygen Enrichment

Cryogenic fluids with a boiling point below that of liquid oxygen have the ability to condense oxygen out of the air if exposed to the atmosphere. This is particularly troublesome if a stable system is replenished repeatedly to make up for evaporation losses; oxygen will accumulate as an unwanted contaminant. Violent reactions (e.g., rapid combustion or explosions) may occur if the system or process is not compatible with liquid oxygen.

Oxygen enrichment will also occur if liquid air is permitted to evaporate. (Oxygen evaporates less rapidly than nitrogen.) Oxygen concentrations of 50% may be reached. Also remember that condensed air dripping from the exterior of cryogenic piping will be rich in oxygen.

Personal Protective Equipment

The potential for freezing by contact with the extreme cold of cryogens necessitates varying degrees of eye, hand, and body protection. When cryogens are spilled, a thin gaseous layer apparently forms next to the skin. This layer protects one from freezing, provided the contact with the cryogens involves small quantities of liquid and brief exposures to dry skin. However, having wet skin or exposure to larger quantities of cryogens for extended periods of time can produce freezing of the tissue.

The most likely cause of frostbite to the hands and body is contact with cold metal surfaces. Because there is no protective layer of gas formed, frostbite will occur almost instantaneously, especially when the skin is moist.

The damage from this freezing (frostbite) occurs as the tissue thaws. Intense hyperemia (abnormal accumulation of blood) usually takes place. In addition, a blood clot may form along with an accumulation of body fluids, which decreases the local circulation of blood. Gangrene may result if the consequent deficiency of blood supply to the affected cells is extreme.

Cooling of the internal organs of the body can also disturb normal functioning, producing a condition known as hypothermia. It is very dangerous to cool the brain or heart to any great extent.

Using safety glasses with side shields is required at all times when cryogenic fluids are present. Goggles provide the best protection for the eyes. If a cryogen is poured or if the fluid in an open container may bubble, a full-face shield is required. This additional protection is also recommended when valves are actuated on piping systems, etc., unless the operator is shielded from leaks at potential failure points.

Hand protection is primarily required to guard against the hazard of touching cold surfaces. Loose, nonasbestos insulating gloves that can be tossed off readily in case they become soaked with cryogen may be worn. Special gloves made for cryogenic work are recommended. Leather gloves, such as welding gloves without the gauntlets, have been used with satisfactory results.

Cryogenic handlers should wear boots and cuffless trousers extending over the boot. Closed-toe shoes that cover the top of the foot shall be worn by all persons handling cryogens. Industrial clothing made of nonabsorbent material is usually satisfactory. Long-sleeved clothing is recommended for arm protection. An apron made of leather or other material recommended for use with cryogens is indicated when large quantities of cryogen are handled. Where exposure to drenching is possible, a full protective suit with supplied air should be considered; however, the system should be engineered to prevent the possibility of such an exposure.

Tongs or other tools should be used to lift objects out of the liquid or liquid baths.

Immediate Treatment for Frostbite

1. Warm the affected area *rapidly* by immersion in water not to exceed 105°F, with body heat, or by exposure to warm air. Safety showers with warm water should be provided where there is a sufficient probability of the occurrence of such an accident. In the event of massive exposure, remove clothing while showering. Do not expose the body to open flame. Maintain the affected area of the victim at normal body warmth until professional help arrives.

2. Calm the victim and avoid aggravating the injury. People with frostbitten feet should not walk on them. Do not rub or massage the affected parts of the body.

3. Prevent infection—use a mild soap to clean the affected area. Dressings need not be applied if the skin is intact.

4. If affected, flush eyes with warm water for at least 15 min.

5. Report to Health Services for medical attention promptly.

Training Procedures and Safety Notes

Cryogenic fluids should be handled only by personnel fully aware of the properties of the materials and equipment. They should be mindful of the consequences of misadventure. Operators should be selected on the basis of capability to understand the hazards and the equipment, mature judgment, and the ability to follow established procedures. A formal training program, work under experienced co-workers, and certification of operators should be considered for larger cryogenic systems. An orientation to cryogenic safety is provided as part of course HS-503, "Pressure Safety Orientation" (4 hr). This course is recommended for all users of cryogens. Material Safety Data Sheets (MSDSs) covering each cryogen being used, handled, or stored shall be immediately available. Copies of the appropriate MSDS shall be posted in the vicinity of the cryogen being used, handled, or stored.

Operational Safety Procedures may be required when cryogenic operations are not authorized by Facility Safety Procedures, when toxic or radioactive materials are used in conjunction with cryogenic systems, or when the system is deemed to pose a serious hazard due to cryogen volume, location, etc. See Supplement 32.03 of the *Health & Safety Manual* for Safety Note requirements.

A simple emergency plan to guide personnel actions during malfunction or mishap is recommended. The plan should cover shut-down, alarm, and evacuation procedures for likely mishaps. Plans that cover every possible exotic mishap are likely to be disregarded entirely.

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